

# Synthesis and Characterization of the First Examples of 1,3,2-Diazastibole and 1,3,2-Diazabismole Ring Compounds

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**ABSTRACT:** Reaction of either 9,10-phenanthrene-dione (phenanthrenequinone) or diphenylethanedione (benzil) with two equivalents of  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ , followed by quenching of the reaction with excess  $\text{Cl-SiMe}_3$ , produces the corresponding  $N,N'$ -bis(trimethylsilyl)- $\alpha$ -diimines in high yields (85–95%). Subsequent dehalosilylation/ring-closure reactions with  $\text{SbCl}_3$  and  $\text{BiCl}_3$  produce, in 90–95% yields, the first examples of 1,3,2-diazaheterole ring compounds containing antimony or bismuth. These 2-chloro-1,3,2-diazaheteroles can be further functionalized at the pnictogen by reaction with, for example,  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ , to produce the corresponding 2-bis(trimethylsilyl)amido-1,3,2-diazaheteroles. All of these new main group element-containing heterocycles have been characterized through  $^1\text{H}$  and  $^{13}\text{C}$  NMR, elemental analysis, and two of the diazastiboles have been structurally characterized by single-crystal X-ray analysis, confirming the ring structures. Both of these diazastiboles exist as associated dimers in the solid state; half of the dimer represents the asymmetric unit.  
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## INTRODUCTION

In recent years, a major emphasis in the synthesis of new main group element-containing compounds

and their chemistry has been in the field of materials science, particularly where such compounds display potentially useful electronic or optical properties [1]. For example, the past three decades have witnessed almost unabated interest in the synthesis and characterization of organic molecular charge-transfer salts, derived to a large extent from the tetrachalcogenofulvalenes, and their applications as superconductors, metals, and magnets [1a–f,i]. Additionally, group 15 element-containing heterocycles have been utilized in the preparation of novel optical materials; Ashe and coworkers have described novel molecular thermochromes based on distiboles and dibismoles [1g].

The motivation behind research on these exotic materials is multifold: (a) the rational design and synthesis of precursor molecules (molecular sub-units), together with reactions to convert these precursors into solid-state materials, pose a challenge to synthetic chemists; (b) in numerous examples, extended solid-state structures have been prepared from such molecular constituents, with the ultimate result of redefining the properties of the solid-state materials through manipulation of the composition and structure of the molecular building blocks; (c) there is a wealth of fundamental solid-state chemistry and physics that has been discovered (and is yet to be discovered) by way of study of such systems; and (d) there are potentially many far-reaching technological applications for such materials within the area of molecular optoelectronic devices.

We have initiated a research program directed toward the synthesis and study of main group ele-

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ment-containing heterocycles: the 1,3,2-diazaheteroles **1** (Scheme 1). Herein we report the synthesis and complete structural characterization of the first examples of 1,3,2-diazastibole ring compounds via a convenient and versatile synthetic route that provides access to a wide variety of structurally related diazaheteroles [2].

This same synthetic strategy has been employed in the preparation of the first 1,3,2-diazabismoles, for which complete spectral characterization is provided as well. Previous attempts at the preparation of 1,3,2-diazastiboles had failed [3]. There is, however, one report of a 1,2,4-diazastibole [4]. Diazaheteroles containing bismuth have never been reported. Examples of 1,3,2-diazaphospholes [4, 5] and a 1,3,2-diazaarsole have been reported previously [4].

## EXPERIMENTAL

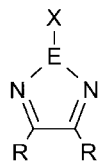
### General Considerations

All manipulations were performed using general Schlenk and/or dry-box techniques. Solvents were appropriately dried and distilled under nitrogen or argon prior to use. Phenanthrenequinone, benzil, lithium bis(trimethylsilyl)amide, antimony trichloride, and bismuth trichloride were all purchased from Aldrich Chemical Company and used as received. All infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded on a Digilab Qualimatic FT-IR. Solid samples were run as pressed potassium bromide pellets. Liquids and oils were pressed as thin films between sodium chloride plates. A Perkin-Elmer Lambda 4C UV-Vis spectrophotometer was employed to obtain electronic absorption spectra (200–800 nm). All samples in this research were dissolved in methylene chloride and placed into 1 cm path length quartz cells with Teflon stoppers. Samples were prepared in the glove box immediately prior to measurement of

the spectra. Proton ( $^1\text{H}$ ) and carbon-13 ( $^{13}\text{C}$ ) nuclear magnetic resonance (NMR) spectra were obtained routinely at 90.0 MHz and 22.5 MHz, respectively, using a JEOL FX-90Q multinuclear magnetic resonance spectrometer. Chemical shift values are reported in parts per million relative to tetramethylsilane. Solid-state  $^{13}\text{C}$  NMR crossed polarization-magic angle spinning (CP-MAS) spectra were obtained at 75.43 MHz on an IBM NR-300 spectrometer, with chemical shift values being reported relative to external *para*-di(*t*-butyl)benzene. Mass spectral data (electron impact ionization) were obtained on a VG 7070 magnetic sector mass spectrometer at an ionizing voltage of 15 eV and referenced to Perfluorokerosene 755. Schwartzkopf Microanalytical Laboratories, Inc. of Woodside, NY, performed all elemental analyses.

### Preparation of Phenanthrenequinone-(9,10)-bis(trimethylsilyl)diimine (**2**).

A benzene solution (~200 mL) of lithium bis(trimethylsilyl)amide (340 mmol), was added via a vented addition funnel to 35.40 g (170 mmol) of 9,10-phenanthrenequinone suspended in 200 mL of benzene, held at 5–10°C. After addition of the amide solution was complete, the temperature of the now homogeneous solution was maintained at 5–10°C for 1 hour, after which the temperature was allowed to slowly warm to 20°C. After 4 hours, the solution color had changed from dark green to deep red. *The change in color is a prerequisite to continue the procedure.* With stirring, the solution was warmed to 70°C for 20 hours. After 20 hours, the solution was cooled to 20°C, and 50 mL (390 mmol) of chlorotrimethylsilane was added via syringe to the stirring solution. Stirring was continued at 60°C for another 5 hours. The solution was then cooled to room temperature and filtered through a medium-porosity Schlenk frit with celite to remove lithium chloride, and the solvent was removed in vacuo. The filtrate was redissolved in 250 mL of toluene to which 75 mL of pentane was also added. The solution was cooled to –78°C for 24 hours. The orange crystalline product was obtained by filtration through a coarse Schlenk frit and subsequently washed with cold pentane (–78°C). A yield of 53.50 g (90%) was obtained, m.p. = 148°C. Anal. calcd (found) for  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{Si}_2$ : C, 68.51% (68.73%), H, 7.47% (7.52%), N, 7.99% (7.91%).  $^1\text{H}$  NMR ( $\delta$ ;  $\text{CD}_2\text{Cl}_2$ ) 7.6–6.6 ppm (multiplet, 8H), 0.2 ppm (s, 18H);  $^{13}\text{C}$ [ $^1\text{H}$ ] NMR ( $\delta$ ;  $\text{CD}_2\text{Cl}_2$ ) 171.1 ppm ( $>\text{C}=\text{N}-$ ), 135.1, 131.8, 128.1, 127.9 123.8 ppm (phenanthro C), 1.4 ppm [ $-\text{Si}(\text{CH}_3)_3$ ]. IR (KBr pellet)  $\nu_{\text{C}=\text{N}} = 1663, 1643\text{ cm}^{-1}$ . MS (EI, 15 eV) [*m/e*



**1**

E = Main Group Element

R = Aryl, Alkyl, CN, *Etc.*

X = Halogen, Alkyl, Aryl, Amido, *Etc.*

SCHEME 1

(relative abundance %): 350 ( $M^+$ , 12.4), 238 (21.9), 237 (100), 207 (24.1), 206 (35.8), 73 ( $-\text{SiMe}_3$ , 68.3), 45 (18.7).

### Preparation of Benzil-bis(trimethylsilyl)diimine (3).

A benzene solution (~200 mL) of lithium bis(trimethylsilyl)amide (340 mmol) was added via a vented addition funnel to 35.7 g (170 mmol) of benzil dissolved in 200 mL of benzene. After addition of the amide solution was complete, the temperature of the solution was maintained at 5–10°C for 1 hour, after which the temperature was allowed to slowly warm to 20°C. Stirring of the deep red solution was continued for 3 hours at 20°C, then for 7 hours at 70°C. The solution was cooled to 20°C, and 50 mL (390 mmol) of chlorotrimethylsilane was added via syringe to the stirring solution. Stirring was continued at 60°C for another 5 hours. The yellow solution was cooled to 20°C and filtered through a medium-porosity Schlenk frit with celite to remove lithium chloride, and the solvent was removed in vacuo. The filtrate was vacuum distilled (b.p. = 150°C, 1 torr) and yielded 57 gm (96%) of yellow crystalline solid (m.p. = 69–70°C). Anal. calcd (found) for  $\text{C}_{20}\text{H}_{28}\text{N}_2\text{Si}_2$ : C, 68.12% (68.52%), H, 8.00% (8.04%), N, 7.94% (7.86%).  $^{13}\text{C}$  NMR ( $\delta$ ;  $\text{CD}_2\text{Cl}_2$ ) 174.7 ppm ( $>\text{C}=\text{N}-$ ), 138.7, 131.6, 128.8, 128.6 ppm (phenyl C), 0.5 ppm [ $-\text{Si}(\text{CH}_3)_3$ ]. IR (KBr pellet)  $\nu_{\text{C}=\text{N}}$  = 1661, 1644  $\text{cm}^{-1}$ . MS (EI, 15 eV) [ $m/e$  (relative abundance %)]: 352 ( $M^+$ , 0.6), 209 (10.0), 179 (20.5), 178 (72.8), 177 (100), 150 (26.1), 148 (10.0), 136 (13.7), 106 (21.0), 105 (38.0), 104 (43.8), 77 (22.6), 76 (19.5), 75 (34.2), 74 (34.5), 73 ( $-\text{SiMe}_3$ , 92.5), 66 (20.5), 55 (24.9).

### Preparation of 2-Chloro-4,5-[9,10-*c*]-phenanthro-1,3,2-diazastibole (4).

In the glove box, (a) 3.50 g (10 mmol) of diimine 2 was placed into a 100 mL Schlenk flask equipped with a magnetic stirring bar and a septum; and (b) 2.28 g (10 mmol) of  $\text{SbCl}_3$  was placed in a solids-addition tube. Freshly distilled benzene (55 mL) was added to the flask containing 2; under a flow of nitrogen, the solids-addition tube was joined to the flask. With stirring, the antimony trichloride was added slowly to the orange diimine solution. The reaction mixture was stirred for 24 hours at room temperature and was subsequently filtered through a medium-porosity Schlenk frit. The precipitate was washed with 20–30 mL of benzene and dried in vacuo. The yield of the orange-brown solid (m.p.

223°C, dec.) was 3.54 g (98%). Anal. calcd (found) for  $\text{C}_{14}\text{H}_8\text{N}_2\text{ClSb}$  (4): C, 46.52% (46.10%), H, 2.23% (2.14%), N, 7.75% (7.58%), Cl, 9.81% (9.97%), Sb, 33.69% (33.81%).

### Preparation of 2-chloro-4,5-diphenyl-1,3,2-diazastibole (5).

Compound 5 was prepared and isolated in a manner identical to 4, in 84% yield. Anal. calcd (found) for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{ClSb}$  (5): C, 46.27% (46.11%), H, 2.77% (2.64%), N, 7.71% (7.60%), Cl, 9.75% (9.91%), Sb, 33.50% (33.61%). CP-MAS  $^{13}\text{C}$  NMR ( $\delta$ ; 75.432 MHz) 172.8 ppm ( $>\text{C} = \text{N}-$ ), 138.7, 136.7, 135.1, 127.9 ppm (phenyl C).

### Preparation of 2-Chloro-4,5-[9,10-*c*]-phenanthro-1,3,2-diazabismole (6).

In the glove box, (a) 3.50 g (10 mmol) of the diimine (2) was placed into a 100 mL Schlenk flask equipped with a magnetic stirring bar and a septum; and (b) 3.15 g (10 mmol) of  $\text{BiCl}_3$  was placed in a solids-addition tube. Freshly distilled benzene (55 mL) was added to the flask containing 2; under a flow of nitrogen, the solids-addition tube was joined to the flask. With stirring, the bismuth trichloride was added slowly to the orange diimine solution. After addition of the solid, a reflux condenser was attached to the flask, and the reaction mixture was refluxed for 24 hours. After refluxing, the solution was cooled and subsequently filtered through a medium-porosity Schlenk frit. The precipitate was washed with 30 mL of tetrahydrofuran, followed by 20 mL of pentane, and dried in vacuo to yield (orange-brown solid, m.p. 204–208°C, dec.) 4.13 g (92%). Anal. calcd (found) for  $\text{C}_{14}\text{H}_8\text{N}_2\text{ClBi}$  (6): C, 37.48% (37.41%), H, 1.80% (1.84%), N, 6.24% (6.28%), Cl, 7.90% (8.09%), Bi, 46.58% (46.81%).

### Preparation of 2-Bis(trimethylsilyl)amido-4,5-[9,10-*c*]-phenanthro-1,3,2-diazastibole (7).

In the glove box, (a) 1.81 g (5 mmol) of 4 was placed in a 100 mL Schlenk flask equipped with a magnetic stir bar and a septum; and (b) 0.84 g (5 mmol) of  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$  was placed in a 50 mL Schlenk flask containing a magnetic stir bar and fitted with a septum. To each flask was added 35 mL of freshly distilled benzene. After the  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$  was completely dissolved in benzene, both flasks were cooled to 6°C, and with the use of a cannula, a slow dropwise addition (1 drop/s) of the amide to the stirred slurry of 4 was initiated. Upon completion of the ad-

dition, the reaction mixture was slowly warmed to 20°C and stirring was continued for an additional 24 hours. The solution was then filtered through a medium-porosity Schlenk frit with celite to remove lithium chloride. The filtrate was dried in vacuo to yield 2.06 g (85%) of the deep red solid **7** (m.p. 124–125°C, dec.).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  169.0 ( $>\text{C} = \text{N}-$ ),  $\delta$  134.6, 134.4, 132.4, 128.7, 123.7 (phenanthro C),  $\delta$  5.2 [ $-\text{Si}(\text{CH}_3)_3$ ]. Anal. calcd (found) for  $\text{C}_{20}\text{H}_{26}\text{N}_3\text{Si}_2\text{Sb}$  (**7**) C, 49.39% (49.52%), H, 5.39% (5.44%), N, 8.64% (8.72%), Sb, 25.03% (25.04%).

#### Preparation of 2-Bis(trimethylsilyl)amido-4,5-diphenyl-1,3,2-diazastibole (**8**).

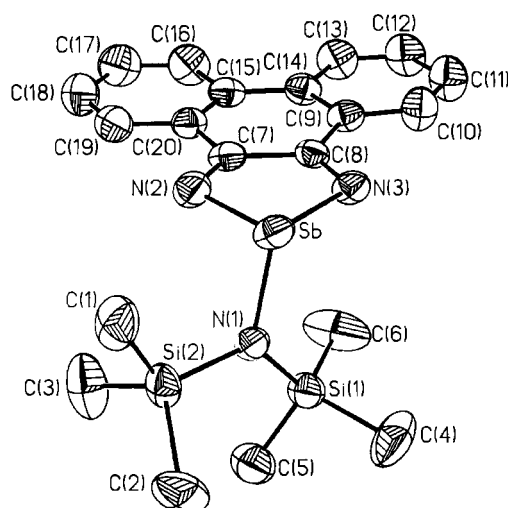
Compound **8** (orange solid) was prepared and isolated in a manner identical to **7**, in 70% yield (m.p. 120°C, dec.). Anal. calcd (found) for  $\text{C}_{20}\text{H}_{28}\text{N}_3\text{Si}_2\text{Sb}$  (**8**) C, 49.19% (49.31%), H, 5.78% (5.84%), N, 8.60% (8.65%), Sb, 24.93% (24.91%).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  176.0 ( $>\text{C} = \text{N}-$ ),  $\delta$  142.2, 129.4, 128.8, 127.9 (phenyl C),  $\delta$  5.8 [ $-\text{Si}(\text{CH}_3)_3$ ].

#### Preparation of 2-Bis(trimethylsilyl)amido-4,5-[9,10-*c*]-phenanthro-1,3,2-diazabismole (**9**).

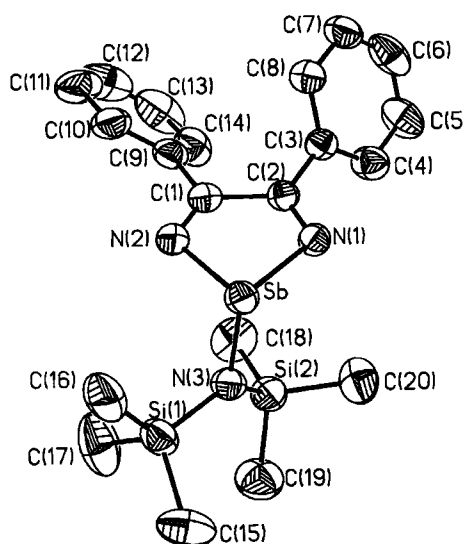
Compound **9** (dark red solid) was prepared and isolated in a manner identical to **7** and **8**, in 85% yield (m.p. 130–135°C, dec.). Anal. calcd (found) for  $\text{C}_{20}\text{H}_{26}\text{N}_3\text{Si}_2\text{Bi}$  (**9**) C, 41.88% (41.72%), H, 4.57% (4.44%), N, 7.33% (7.42%), Bi, 36.43% (36.31%).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  174.6 ( $>\text{C} = \text{N}-$ ),  $\delta$  149.5, 135.8, 131.9, 128.2, 126.9, 124.2 (phenanthro C),  $\delta$  5.7 [ $-\text{Si}(\text{CH}_3)_3$ ].

#### X-RAY STRUCTURAL SOLUTION AND REFINEMENT

X-ray data were collected on an upgraded Syntex P2<sub>1</sub> diffractometer. Deep red crystals of **7** and bright orange crystals of **8**, grown by vapor diffusion (pentane into  $\text{CH}_2\text{Cl}_2$ ) and suitable for x-ray diffraction, were mounted in glass capillaries in the glove box under argon. The unit cell parameters were obtained by the least-squares refinement of the angular settings of 27 reflections ( $27^\circ < 2\theta < 33^\circ$ ). The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures [6]. All software and sources of the scattering factors were contained in the Nicolet SHELXTL program library. ORTEP diagrams showing the solid-state structures and atom-numbering schemes are given in Figures 1 and 2. Crystallographic data are summarized in Tables 1 and 2, and selected bond lengths and bond angles are presented in the figure captions.



**FIGURE 1** ORTEP view of **7**, showing the atomic numbering schemes. Selected bond lengths (Å) and angles (deg): Sb–N(2) 2.093(3), Sb–N(3) 2.098(3), Sb–N(1) 2.049(3), C(7)–N(2) 1.282(5), C(8)–N(3) 1.292(5), C(7)–C(8) 1.533(5), N(2)–Sb–N(3) 83.1(1), N(1)–Sb–N(2) 91.5(1), N(1)–Sb–N(3) 105.9(1), C(7)–N(2)–Sb 109.6(3), C(8)–N(3)–Sb 109.0(2), N(2)–C(7)–C(8) 119.1(3), and N(3)–C(8)–C(7) 118.9(3).



**FIGURE 2** ORTEP view of **8**, showing the atomic numbering schemes. Selected bond lengths (Å) and angles (deg): Sb–N(2) 2.103(3), Sb–N(1) 2.096(3), Sb–N(3) 2.040(3), C(1)–N(2) 1.261(5), C(2)–N(1) 1.265(4), C(1)–C(2) 1.557(7), N(1)–Sb–N(2) 82.0(1), N(2)–Sb–N(3) 94.5(1), N(1)–Sb–N(3) 104.6(1), C(1)–N(2)–Sb 110.6(3), C(2)–N(1)–Sb 110.1(3), N(2)–C(1)–C(2) 118.1(3), and N(1)–C(2)–C(1) 118.5(4).

#### RESULTS AND DISCUSSION

The synthetic approach to the new diazastibole and diazabismole ring compounds described herein centers on the dehalosilylation/ring closure reaction of the appropriate diazabutadiene ( $\alpha$ -diimine) with the

**TABLE 1** Crystallographic Data Collection Parameters for 2-Bis(trimethylsilyl)amido-4,5-[9,10-*c*]phenanthro-1,3,2-diazastibole (**7**)

<b>7</b>	
Molecular formula	C <sub>20</sub> H <sub>26</sub> N <sub>3</sub> Si <sub>2</sub> Sb
Formula weight	486.30
Crystal system	P2 <sub>1</sub> /c
Space group	monoclinic
<i>a</i> (Å)	12.406(2)
<i>b</i> (Å)	21.237(3)
<i>c</i> (Å)	8.190(2)
$\beta$	91.512(1)
<i>V</i> (Å <sup>3</sup> )	2157.0(7)
<i>Z</i>	2
Radiation (wavelength, Å)	Mo-K $\alpha$ (0.71073)
Scan mode	$\omega$
$\mu$ (cm <sup>-1</sup> )	14.04
Temp (°C)	293
<i>D</i> <sub>calcd</sub> (g·cm <sup>-3</sup> )	0.7490
Crystal dimensions (mm)	0.15 × 0.25 × 0.14
Reflections collected	4790
Independent reflections	3734
<i>R</i> ; <i>R</i> <sub>w</sub> <sup>a</sup>	0.0420, 0.0359

<sup>a</sup>Function minimized:  $\sum w(|F_o| - |F_c|)^2$ .

**TABLE 2** Crystallographic Data Collection Parameters for 2-Bis(trimethylsilyl)amido-4,5-diphenyl-1,3,2-diazastibole (**8**)

<b>8</b>	
Molecular formula	C <sub>20</sub> H <sub>28</sub> N <sub>3</sub> Si <sub>2</sub> Sb
Formula weight	488.32
Crystal system	P2 <sub>1</sub> /c
Space group	monoclinic
<i>a</i> (Å)	12.819(2)
<i>b</i> (Å)	14.901(3)
<i>c</i> (Å)	13.631(3)
$\beta$	114.98(1)
<i>V</i> (Å <sup>3</sup> )	2157.0(8)
<i>Z</i>	2
Radiation (wavelength, Å)	Mo-K $\alpha$ (0.71073)
Scan mode	$\omega$
$\mu$ (cm <sup>-1</sup> )	12.83
Temp (°C)	293
<i>D</i> <sub>calcd</sub> (g·cm <sup>-3</sup> )	0.6874
Crystal dimensions (mm)	0.17 × 0.26 × 0.20
Reflections collected	4534
Independent reflections	3232
<i>R</i> ; <i>R</i> <sub>w</sub> <sup>a</sup>	0.0393, 0.0264

<sup>a</sup>Function minimized:  $\sum w(|F_o| - |F_c|)^2$ .

requisite pnictogen trihalide (Scheme 2). The  $\alpha$ -diimines used for the work described herein were first reported by Tuchtenhagen and Rühlmann [5], and their syntheses have been modified allowing for significant improvements in yield. Thus, phenanthrenequinone-(9,10)-bis(trimethylsilyl)diimine **2** and benzil-bis(trimethylsilyl)diimine **3** were prepared by

the reactions of phenanthrenequinone and benzil, respectively, with two equivalents of lithium bis(trimethylsilyl)amide followed by quenching with chlorotrimethylsilane. In the original report, compound characterization was based only upon elemental analysis, and the yield for **2** was modest, at 34%. Complete spectroscopic characterization is provided herein.

The diimines were subsequently reacted with SbCl<sub>3</sub> to yield 2-chloro-4,5-[9,10-*c*]phenanthro-1,3,2-diazastibole **4**, and 2-chloro-4,5-diphenyl-1,3,2-diazastibole **5**, respectively. Analogously, **2** reacted with BiCl<sub>3</sub> to yield 2-chloro-4,5-[9,10-*c*]phenanthro-1,3,2-diazastibole **6**.

Due to insolubility in most solvents (i.e., acetone, acetonitrile, benzene, chloroform, diethyl ether, toluene), and reactivity toward others (e.g., DMSO, pyridine), solution-phase NMR data were not obtained for either **4**, **5** or **6**. However, CP-MAS <sup>13</sup>C NMR data were obtained for **5**, providing verification of the structure. All four phenyl carbons are well resolved, and the imine carbon is observed at  $\delta$  172.8 ppm, relative to external *p*-di(*t*-butyl)benzene. The 2-chloro-1,3,2-diazabismole compound **6** was similarly insoluble in all solvents examined, which prevented obtaining spectral data for characterization purposes. Attempts to obtain mass spectral (electron impact ionization) data on the 2-chloro- and 2-amido-1,3,2-diazaheteroles (compounds **4**–**9**) were unsuccessful because no molecular ions were observed.

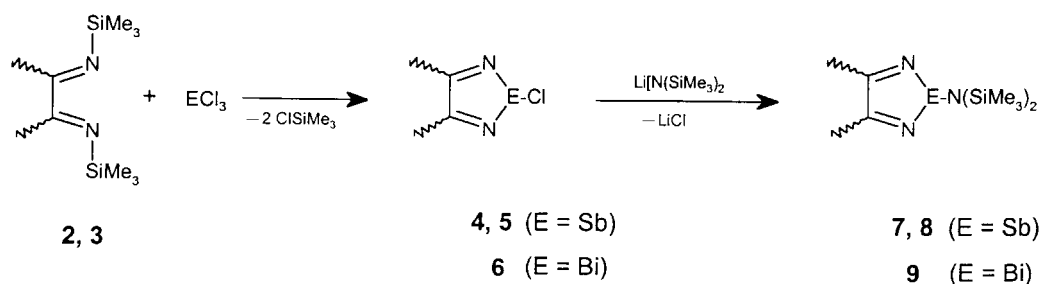
Ultimately, both of the 2-chloro-1,3,2-diazastiboles (**4,5**) and the 2-chloro-1,3,2-diazabismole (**6**) were converted, by reaction with lithium bis(trimethylsilyl)amide, to the corresponding 2-bis(trimethylsilyl)amido-1,3,2-diazastiboles (**7,8**), and the corresponding 2-bis(trimethylsilyl)amido-1,3,2-diazabismole (**9**). The structures of **7** and **8** have been confirmed by X-ray crystallography. The molecular structures are shown in Figures 1 and 2. Inspection of the X-ray diffraction data reveals a number of features that serve to define these new ring compounds. First, in **7**, the bond distances between C(7)–N(2) and C(8)–N(3) are 1.282(5) and 1.292(5) Å, respectively, and in **8**, the bond distances between C(1)–N(2) and C(2)–N(1) are 1.261(5) and 1.265(4) Å, respectively; in both instances these bond distances are characteristic of C = N double bonds as found in oximes and imines [7]. Second, in **7**, the bond angles N(1)–Sb–N(2), N(1)–Sb–N(3), and N(2)–Sb–N(3) are 91.5(1)°, 105.9(1)° and 83.1(1)°, respectively, and in **8** the corresponding bond angles N(2)–Sb–N(3), N(1)–Sb–N(3), and N(2)–Sb–N(1) are 94.5(1)°, 104.6(1)°, 82.0(1)°, respectively; in both instances, angles suggesting that the antimony uses

primarily p orbitals in bonding. Third, in **7**, the Sb–N(2) and Sb–N(3) (Sb–N<sub>Ring</sub>) distances are 2.093(3) and 2.098(3) Å, respectively, while in **8** the Sb–N(2) and Sb–N(1) distances are 2.103(3) Å and 2.096(3) Å, respectively; these distances are similar to the Sb–C<sub>Ring</sub> distances found in a structurally similar distibole (isoelectronic C<sub>4</sub>Sb ring) reported by Ashe [8].

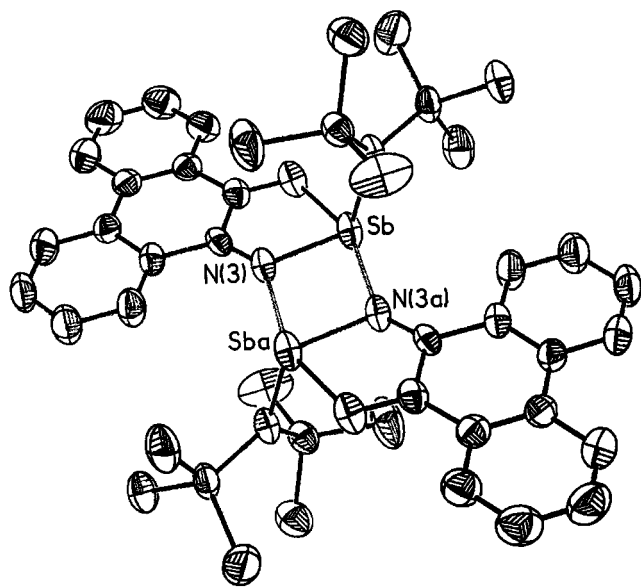
As illustrated in Figures 3 and 4, both of these diazastiboles exist as associated dimers in the solid state; half of the dimer represents the asymmetric unit. ORTEP drawings with the atomic numbering scheme and selected bond lengths and angles are shown in Figures 3 and 4. There are relatively strong intermolecular attractions in both dimers with Sb–N distances of 2.744(5) Å for **7** and 2.846(5) Å for **8**, versus 3.70 Å for the sum of the van der Waals radii of these atoms. This association in the solid state probably accounts for the somewhat canted (tri-

methylsilyl)amido-groups, as reflected by the difference observed for **7** in the N(1)–Sb–N(2) and N(1)–Sb–N(3) bond angles of 91.5° and 105.9°, respectively; analogous differences are observed for **8** in the N(2)–Sb–N(3) and N(1)–Sb–N(3) bond angles of 94.5(1)° and 104.6(1)°, respectively. These dimers are analogous to a recently reported telluradiazole that exists also in the solid state as an association dimer [9], and the parent molecule 1,2,5-telluradiazole that exhibits a ribbon polymeric structure in the solid state [10].

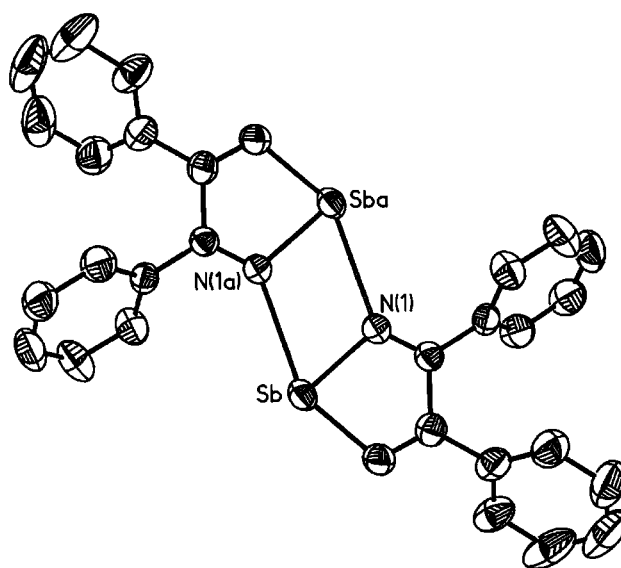
The synthetic strategies described herein, namely conversion of  $\alpha$ -diketones to the corresponding  $\alpha$ -diimines and subsequent dehalosilylation/ring closure reaction between the *N,N'*-bis(trimethylsilyl)- $\alpha$ -diimine and a polyhaloelement (EX<sub>n</sub>) species, are proving to be of general synthetic applicability, providing access to novel diazaheteroles that



SCHEME 2



**FIGURE 3** ORTEP diagram and atomic numbering scheme for the association dimer of **6**. Selected bond lengths and angles: Sb–N(3a) 2.744(3) Å, N(1)–Sb–N(3a) 91.2°(2), N(2)–Sb–N(3a) 155.1°(3), N(3)–Sb–N(3a) 72.3°(2).



**FIGURE 4** ORTEP diagram and atomic numbering scheme for the association dimer of **7** [bis(trimethylsilyl)amido groups omitted for clarity]. Selected bond lengths and angles: Sb–N(1a) 2.846(3) Å, N(1)–Sb–N(1a) 67.5°(2), N(2)–Sb–N(1a) 149.2°(2), N(3)–Sb–N(1a) 97.3°(2).

contain a variety of main group elements and have widely varying substituents and physical/chemical properties [2]. These developments will be the subject of future publications.

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